7-69611

* NOTICES *

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CLAIMS

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(57) [Claim(s)]
[Claim 1] A pattern formation method characterized by having a process which forms the 1st organic compound film containing an acid generator on a base, a process which forms spreading glass membrane on said 1st organic compound film, a process which forms a chemistry multiplier system resist film on said spreading glass membrane, and a process which exposes said chemistry multiplier system resist film, and forms a desired pattern.
[Claim 2] Said acid generator is the pattern formation method according to claim 1 characterized by being an onium salt, a sulfonate, or a halogenated compound.
[Claim 3] A pattern formation method characterized by having a process which forms spreading glass membrane on said antireflection film, a process which forms a chemistry multiplier system resist film on said spreading glass membrane, and a process which exposes said chemistry multiplier system resist film, and forms a desired pattern.
[Claim 4] A pattern formation method characterized by having a process which forms the 1st chemistry multiplier system resist film on a base, a process which forms spreading glass membrane on said 1st chemistry multiplier system resist film, a process which forms the 2nd chemistry multiplier system resist film on said spreading glass membrane, and a process which exposes said 2nd chemistry multiplier system resist film, and forms a desired pattern.
[Claim 5] A pattern formation method characterized by providing the following. A process which forms the 1st chemistry multiplier system resist film on a base The 1st baking process of baking said 1st chemistry multiplier system resist film A process which forms spreading glass membrane on said 1st chemistry multiplier system resist film A process which forms said 1st chemistry multiplier system film and 2nd chemistry multiplier system resist film of this material on said spreading glass membrane, the 2nd baking process of baking said 2nd chemistry multiplier system resist film on different conditions from the 1st baking process, and a process which exposes said 2nd chemistry multiplier system resist film, and forms a desired pattern
[Claim 6] A pattern formation method characterized by having a process which forms a silicon resin film containing an acid generator on a base, a process which forms a chemistry multiplier system resist film on said silicon resin film, and a process which exposes said chemistry multiplier system resist film, and forms a desired pattern.
[Claim 7] A pattern formation method characterized by having a process which forms spreading glass containing an acid generator on a base, a process which forms a chemistry multiplier system resist film on said spreading glass membrane, and a process which exposes said chemistry multiplier system resist film, and forms a desired pattern.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the lithography technology in ULSI manufacture etc., especially relates to the pattern formation method using a chemistry multiplier system resist.
[0002]
[Description of the Prior Art] High accumulation and densification of ULSI are advanced with 4 times as many vigor as this in 3, and it has already succeeded in fertilization of 4-megabit DRAM, and the prototype of a 16 megabit DRAM. The size required of micro processing in connection with this is increasingly made detailed to 0.8 micrometers to 0.5 micrometers, and 0.5 more micrometers or less. Since it corresponds to the trend of detailed-izing, examination which improves definition in various lithography technology is advanced.
[0003] The pattern formation method of using the light of short wavelength further from the light conventionally used for mass production for the improvement in definition is examined by the phot lithography which is the mainstream of current lithography. However, since the absorption of light within a resist material becomes high by short wavelength-ization, it is a problem that the configuration of a pattern tends to deteriorate. In order to solve this problem, the resist material of high light transmittance is needed. Moreover, in the electron beam lithography which bears the next generation, in order to improve low productivity, a resist material of high sensitivity is desired.
[0004] recently JIE . back . SAI . TEKUNORU . BI 6 (1), and Jean /FEBU " -- nano lithography [ ] -- the Wiz -- Anh acid KATARAIZUDO resist" '88 PIPI 319-322 (J.Vac.Sci.Technol.B6 (1) --) Jan/Feb'88pp 319-322, "Nanolithography with an acid catalyzedresist" and this pp 379-383, Characterization OBU A yes - RIZORYUSHON Novolak Based one Negative EB resist 4 microcoulomb / SUKYUA cm Wiz () ["Characterization of a high-resolution novolak based negative electron-beam] The new high performance resist material using a chemistry amplification reaction, i.e., a catalysis, is capturing the spotlight as stated also to resist with 4microC/cm2 sensitivity."
[0005] The material which generates the matter used as a catalyst is newly contained in the resist material using this chemistry amplification reaction by the exposure of an energy line, the intermediate product produced by the exposure of an energy line serves as a catalyst of the reaction of a resist at the time of down stream processing, such as subsequent heat-treatment, and there is the feature that a reaction progresses efficiently. For this reason, compared with the conventional resist material, permeability and sensitivity of a resist can be made high.
[0006]
[Problem(s) to be Solved by the Invention] However, it is spreading mold glass (what takes siloxane structure as generally indicated to be spreading glass to drawing 8 is said.) about said chemistry multiplier system resist. Here, Z1 and Z2 can become an alkyl group, an alkoxy group, an acetoxy radical, a hydroxyl group, hydrogen, or a siloxane compound, respectively. Moreover, n expresses the number of average condensation of spreading glass. When applied upwards, it became clear in an artificer's etc. experiment to produce abnormalities in a resist pattern cross-section configuration. The

abnormality phenomenon in a configuration of this resist cross section is a problem which arises since the catalyst matter in a resist material decreases in number near [a substrate material] this and ununiformity distribution of the catalyst matter arises in the direction of resist thickness. In the negative resist in which the portion which irradiated especially the energy line remains, in order for unusual interlocking to arise into the base portion of a pattern, and for a resist pattern to fall on it and to carry out induction of the ** separation to it, it is the important problem which must be solved. This phenomenon is explained in more detail using drawing 2 .

[0007] When processing a resist using the three-layer resist method which arranges spreading mold glass 203 to the film 204 for acid resisting and the middle class who turn into a lower layer from an organic compound, and arranges the chemistry multiplier system resist 202 of a negative mold in the upper layer, the catalyst matter 205 arises into the portion which irradiated the energy line 201, and the latent image of a pattern is formed. However, with spreading mold glass 203, in order that the catalyst matter 205 in this resist 202 may decrease in number, the portion 206 to which the catalyst matter was missing in this resist 202 arises. Therefore, the distribution condition of the catalyst matter inside this resist becomes an ununiformity as shown in (a). Since bridge formation does not take place about the portion which lacked the catalyst matter in order to serve to stimulate crosslinking reaction, as shown in (b), abnormalities produce the catalyst matter in the cross-section configuration after resist development. For this reason, the class of furring which can be set as the application object of a chemistry multiplier system resist is narrowed remarkably, and utilization of the ULSI manufacture field becomes difficult.

[0008] Then, this invention cancels the abnormality interlocking phenomenon of such a pattern cross section, and aims at attaining wide use of the above-mentioned resist material application irrespective of the material of a substrate.

[0009]

[Means for Solving the Problem] The above-mentioned object is attained by using a material containing a generating agent of matter used as a catalyst for spreading glass which should carry out paint film formation of said resist, or a spreading glass lower layer, when applying a resist material of chemistry amplification (catalyst) reaction utilization. Generally an acid generator is used as a generating agent of matter used as a catalyst in many cases, using an acid as this catalyst. By explanation, a material of this acid-catalyst system will be used below.

[0010]

[Function] The aiming at phase murder and normal pattern formation cure-by a certain method method to reduction of the acid in a resist with spreading mold glass was examined. This is explained using drawing 1 below.

[0011] When preparing the layer of the organic compound 4 which contained the acid generator in the lower layer of this spreading mold glass 3 as shown in (a), and processing the chemistry multiplier system resist 2, if an energy line 1 is irradiated, an acid 5 will be generated in a resist 2. Simultaneously, when this energy line 1 reaches in this organic compound film 7, an acid 5 is generated also in this organic compound film 7. Since the acid which is equivalent to a part [missing] within this resist 2 is compensated from the acid 5 diffused from the film of this lower layer organic compound, distribution of concentration stops here, producing it in the acid 5 in a resist 2. Naturally, in a result, as shown in (b), the pattern configuration of this resist 2 can acquire the normal rectangle cross-section configuration which is satisfactory in any way.

[0012] It checked that there was an operation which can normalize said pattern cross-section configuration by using for furring of spreading mold glass the layer of the organic compound which contains an acid generator as mentioned above.

[0013] In addition, as an acid generator, an onium salt, a sulfonate, a halogenated compound, etc. can be used, for example.

[0014]

[Example]

(Example 1) The 1st example is an example of the cure against the abnormalities in a cross section when an optical absorption coefficient uses the base resin of the organic system of 1 as a lower layer film

(antireflection film) of a three-layer resist in general which added the photo-oxide generating agent 5% to the solution. Details are explained using drawing 3 below.
[0015] 1.6-micrometer paint film formation of the base resin 304 of this organic system is carried out on the processed substrate 307, and and the material was made to insolubilize 230 degrees C with hot plate type BEKU equipment. [for 6 minutes] Subsequently, paint film formation of the spreading glass 303 was carried out on this, and similarly, and eburnation of the material was carried out. [230 degrees C] [for 6 minutes] Hydrophobing processing was performed before spreading of the upper resist. Then, paint film formation of chemistry multiplier system negative-mold photoresist THMR-i100 (Tokyo adaptation make) 302 is carried out, and with this equipment, and 90 degrees C of solvents were volatilized. [for 2 minutes] For the exposure 301 of a pattern, using i line cutback projection aligner (NA=0.42), as it was in (a), the desired pattern was imprinted. Furthermore, BEKU after exposure was performed for 2 minutes at 110 degrees C, and by developing negatives with the solution of 2.38% of tetramethylammonium hydroxide concentration, as shown in (b), the pattern was formed. When the above-mentioned resist pattern cross section was observed with the scanning electron microscope, in the pattern cross section, the good rectangle cross section where it is normal in any way has been checked. In addition, the range of an optical absorption coefficient can be used by 0.02-2. However, as for the range of the geometry precision of a pattern, and the field of stability to an optical absorption coefficient, 0.08-1.2 are more desirable.
[0016] (Example 2) The 2nd example is an example at the time of using chemistry multiplier system resist SAL601 (Shipley Far East company make) 402 for the upper layer, it using this resist THMR-i100 (404) for the middle class at this spreading glass 403 and a lower layer material, and performing the cure against the abnormalities in a pattern cross section. Details are explained using drawing 4 below. This THMR-i100 (404) and spreading glass (403) performed 230 degrees C and BEKU for 6 minutes after spreading, respectively. Subsequently, using electron-beam-lithography equipment with an acceleration voltage of 30kV, as shown in (a), the desired pattern was exposed, after performing surface hydrophobing processing, spreading, 80 degrees C, and software BEKU for 30 minutes (401). After that, in BEKU processing and the development by the tetramethylammonium hydroxide (0.27 conventions) solution, as shown in (b), the pattern was formed. The good rectangle cross section where it is normal in any way was obtained like the example 1 in the pattern cross section.
[0017] (Example 3) An example 3 is an example at the time of newly carrying out paint film formation of chemistry multiplier system negative-mold photoresist material THMR-i100 (Tokyo adaptation make) 502 under spreading glass with the upper material of a multilayer-resist method, and performing the cure against the abnormalities in a cross section of a pattern with four-layer resist structure. Details are explained using drawing 5 .
[0018] 1.6-micrometer paint film formation of the optical absorption nature lower layer material (Hitachi Chemical trade name: RAYCAST (RB3900B)) 508 of an organic system is carried out as a film for acid resisting of light on the processed substrate 507, and and the material was made to insolubilize 230 degrees C with hot plate type BEKU equipment. [for 6 minutes] Subsequently, paint film formation of resist THMR-i100 (504) was carried out, and the material was made to insolubilize similarly. Besides the spreading glass material (503) was applied, similarly, and eburnation of the material was carried out. [230 degrees C] [for 6 minutes] Hydrophobing processing was performed before spreading of the upper resist. Then, paint film formation of resist THMR-i100 (502) is carried out, and with this equipment, and 90 degrees C of solvents were volatilized. [for 2 minutes] For exposure of a pattern, using i line cutback projection aligner (NA=0.42), as shown in (a), the desired pattern was imprinted using i line (501). Furthermore, BEKU after exposure was performed for 2 minutes at 110 degrees C, and by developing negatives with the solution of 2.38% of tetramethylammonium hydroxide concentration, as shown in (b), the pattern was formed. When the above-mentioned resist pattern cross section was observed with the scanning electron microscope, there are no abnormalities in a pattern cross section in any way, and even the detailed pattern was able to be processed in the good rectangle cross-section configuration.
[0019] (Example 4) The 4th example is an example which formed the resist pattern for the silicon resin

which added acid generator triphenylsulfonium triflate as the middle class of a three-layer resist. Details are explained using drawing 6 .
[0020] This acid generator of 5% of amount was added to the solid content of the glass of this silicon resin solution that uses a methanol as a principal component, and 0.1-micrometer paint film formation of this silicon resin (603) was carried out on the silicon substrate (607). In addition, 604 is the antireflection film of an organic system. Subsequently, and the solvent of this silicon resin (603) was volatilized. [the temperature of 200 degrees C] [for 30 minutes] Hydrophobing surface treatment was performed to this, paint film formation of chemistry multiplier system resist material SAL601 (Shipley Far East company) 602 was carried out by 0.5-micrometer thickness, and with electron-beam-lithography equipment with an acceleration voltage of 30kV, as shown in (a), the pattern was drawn using the electron ray (601). Furthermore, BEKU after exposure was performed for 10 minutes at 110 degrees C, and by developing negatives with the solution of tetramethylammonium hydroxide (0.27 conventions), as shown in (b), pattern formation was carried out. When the above-mentioned resist pattern cross section was observed with the scanning electron microscope, there are no abnormalities in a pattern cross section in any way, and the good rectangle cross section was able to be formed.
[0021] (Example 5) The 5th example is an example at the time of using for the lower layer material of a positive type chemistry multiplier system resist the material which added 5% of amount for acid generator triphenylsulfonium triflate to the solid content of this spreading glass on titanium system spreading glass. It explains using drawing 7 .
[0022] The laminating of the spreading glass material (703) which added the above-mentioned acid generator was carried out on the processed substrate (704), the laminating of this positive resist (702) was further carried out to the upper layer, and when it exposed using an electron ray (701) and a pattern was formed, also in (a), the problem of the abnormalities in a cross section as well as an example 1 has been solved (b).
[0023] Moreover, according to this example, if pattern processing of the positive type chemistry multiplier system resist which consists of novolak resin, a dissolution inhibitor, and an acid generator is carried out on the spreading glass membrane of the mixed stock of a titanic-acid ghost and a silicon oxide, the problem which a resist base portion insolubilizes can be coped with.
[0024] In addition, since the concept of this invention is in the method of avoiding the abnormalities in a cross-section configuration of a chemistry multiplier system resist with the material containing an acid generator, if it is the material which can add an acid generator, it cannot be overemphasized not only paint film type silicon resin or spreading glass but that other furring may be used.
[0025]
[Effect of the Invention] According to this invention, the abnormalities in a cross-section configuration of the chemistry multiplier system resist pattern resulting from a certain kind of substrate material can be avoided, without adding complicated processing to the conventional multilayer-resist process in any way. The class of acid of the chemistry multiplier system resist of the upper layer in this case and a content hope that it is not necessarily the same, if the combination of what is contained into the material prepared in a lower layer is taken into consideration. Moreover, also in materials other than this, although only the cure method of the abnormalities in a pattern cross section which happens by disappearance of the acid of a chemistry multiplier system resist was described, when it originates in volatilization or diffusion of the matter in a material and an abnormality phenomenon arises, it is the same concept as this invention of compensating the matter which disappeared from a lower layer material, and the same effect is acquired this time. For this reason, engine performance, such as a chemistry multiplier system resist using the reaction of semiconductor devices, such as ULSI to be integrated highly increasingly from now on, or the catalyst matter used [overly] for manufacture of a detailed device, can be pulled out effectively, and the further advancement of these elements is promoted powerfully.

[Translation done.]